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 TI **Solder** containing **tin**, **zinc**, and additional
 components
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AB A **Sn**-based **solder** contains 3-21% **Zn** and
 .ltoreq.0.5% addnl. component with a vapor pressure higher than that of
Zn. Examples of the addnl. components which are in a solid form
 at normal temp. and under normal pressure include Be, Mg, Ca, Sr, Ba, Mn,
Ga, In, Ta, P, Sb, Bi, S, Se, Te, and Po. Other examples include
 Sc, Y, La, Ti, Zr, Cr, Fe, Co, Ni, Cu, **Ag**, B, **Al**, Si,
 and N.

PATENT ABSTRACTS OF JAPAN

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(54) SOLDERING MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a tin-zinc soldering material in which a solder paste high in preservation is prepared, and a solder junction less in secular change is formed.

SOLUTION: A soldering material contains, by weight, tin, 3-21% zinc to the tin, and a small amount of substances to be added. The substances to be added include the contents of $\leq 0.05\%$ of the total amount which are selected among beryllium, magnesium, calcium, strontium, barium, manganese, gallium, indium, thallium, phosphor, antimony, bismuth, sulfur, selenium, tellurium, and polonium, and is solid at normal temperature and normal pressure, and higher than zinc in vapor pressure, or contents to be selected among scandium, yttrium, lanthanum, titanium, zirconium, chromium, iron cobalt, nickel, copper, silver, boron, aluminum, silicon and nitrogen.

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CLAIMS

[Claim(s)]

[Claim 1] It is the pewter material which contains the zinc of 3 - 21% of the weight of a rate, and an addition component with vapor pressure are a solid-state in an ordinary temperature ordinary pressure, and higher than zinc, and is characterized by containing this addition component at 0.5 or less % of the weight of a rate to the pewter material whole quantity to tin and tin.

[Claim 2] The aforementioned addition component is pewter material according to claim 1 chosen from the group which consists of beryllium, magnesium, calcium, strontium, barium, manganese, a gallium, an indium, a thallium, phosphorus, antimony, a bismuth, sulfur, a selenium, a tellurium, and a polonium.

[Claim 3] Pewter material according to claim 1 which contains the aforementioned zinc at 7 - 13% of the weight of a rate to tin.

[Claim 4] It is the pewter material which contains tin and the addition component chosen from the group which consists of the zinc, a scandium, an yttrium and a lanthanum, the titanium, the zirconium, the chromium, the iron, the cobalt, the nickel, the copper, the silver, the boron, the aluminum, silicon, and nitrogen of 3 - 21% of the weight of a rate to tin, and is characterized by containing this addition component at 0.5 or less % of the weight of a rate to the whole quantity.

[Claim 5] Pewter material according to claim 4 which contains the aforementioned zinc at 7 - 13% of the weight of a rate to tin.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the pewter material which does not contain the lead for joining the electrical and electric equipment, an electron, or a machine part. In detail, it is related with the pewter material containing the joinable tin and joinable zinc of a high metallic material of the versatility of the electrical and electric equipment or electronic parts, such as the circuit board, stainless steel, etc.

[0002]

[Description of the Prior Art] Soldering is the technology in which the melting point joins bodies using the comparatively low matter, it is used for many years and it is said that the origin can go back to the old Mesopotamia civilization. In present-day industry, soldering is broadly used for junction of electronic equipment, and assembly. For example, it is used for the junction for mounting electronic parts, such as a semiconductor, a microprocessor, memory, and resistance, in a substrate etc. in the mounting substrate. The advantage of soldering is that electrical installation is formed of the conductivity of the metal contained in a pewter, and it not only fixes parts to a substrate, but differs from the adhesives of an organic system in this point.

[0003] The pewter generally used is a eutectic pewter by tin and lead, and the theoretical eutectic point is 183 degrees C, and rather than the temperature to which much thermosetting resin begins gasification, for the low reason, tin / lead eutectic pewter is used for junction of a substrate etc., and it has the feature that it is not necessary to damage a printed circuit board etc. with heat. Moreover, a tin component forms a characteristic metallic-compounds layer by the interface of a copper plate, and, as for this eutectic pewter, strengthening adhesive strength of a pewter and copper more is also known.

[0004] The eutectic pewter by tin and lead equipped with such a feature is important in junction of the parts in manufacture of electronic equipment, and assembly. thick-film formation and a conductor -- in detailed soldering processing like circuit formation and semiconductor mounting, the screen-stencil method using the solder paste of the shape of a paste which mixed pewter powder and flux etc. is used, and the need of the pewter in the mounting technology of electronic parts is growing increasingly as the rapid spread of the personal devices represented by a personal computer, a cellular phone, the pager, etc. progresses

[0005] The spread of electronic equipment lives a life of people rich. On the other hand, it is also a fact that the electronic equipment which it stopped using is discarded so much, and it is doubtful of the environmental problem by waste arising. For this reason, the manufacture-method of not using recycling use or the detrimental matter of waste is advocated. From a viewpoint of preventing environmental pollution, especially exclusion of a toxic substance is desirable and it is thought also in the junction technology by the pewter that it needs development.

[0006]

[Problem(s) to be Solved by the Invention] Although tin / lead eutectic pewter has the special feature that the wettability to a base material is superior to other metal mixture, when the lead contained in this pewter reclaimed land from and disposes of the discarded electronic equipment, we are anxious about lead ion being eluted into soil by being exposed to acid rain etc. over many years. Since it corresponds to this, although the technology which fixes lead is proposed, sufficient data over a long period of time are not obtained about

diffusion into soil. Furthermore, according to the densification of the latest memory device, a close-up of the influence on the electronic equipment by lead is taken, and reexamination is [as opposed to / leaden use / from the field of the correspondence to the high density assembly in a semiconductor device] needed.

[0007] From such a situation, the junction technology using the pewter which does not contain lead is needed. However, since neither the pewter which replaced lead with other metals, nor the pewter by the combination of another metal becomes so sufficient that it is used so much as a general-purpose product thing about the property needed for pewters, such as wettability, soldering temperature, material strength, and economical efficiency, it is a grade it is expected that the use which did not yet result in spread but was limited to the specific use is.

[0008] Since equipment and the facility of a screen-stencil method using a solder paste have permeated the manufacture site in junction and assembly of the electrical and electric equipment and electronic parts in the present condition, utilization of the solder paste of the pewter which does not contain lead is called for. However, now, most unleaded solder pastes are not put [that utilization of the solder paste in the pewter of complicated 3 yuan or more systems, such as tin / silver / bismuth pewter, is only tried slightly, and] in practical use. It is mentioned that the solder paste which has the shelf life of this reason satisfied with one is not obtained. Furthermore, there are also problems, such as aging of the pewter after junction, i.e., change of a mechanical characteristic etc.

[0009]

[Means for Solving the Problem] Then, in order that this invention persons may solve the environmental problem by the lead in waste As a result of repeating research wholeheartedly about soldering using the pewter by the high metal of the versatility which does not contain lead, by carrying out minute amount addition of the specific third component It finds out that improvement in the stability of the tin-zinc pewter at the time of preparing to a solder paste and aging of the tin-zinc pewter after junction can be suppressed, and came to complete the pewter material of this invention.

[0010] The pewter material of this invention is [in / the zinc and the ordinary temperature ordinary pressure of 3 - 21% of the weight of a rate / to tin and tin] a solid-state, an addition component with vapor pressure higher than zinc is contained, and this addition component is contained at 0.5 or less % of the weight of a rate to the pewter material whole quantity.

[0011] The above-mentioned addition component is chosen from the group which consists of beryllium, magnesium, calcium, strontium, barium, manganese, a gallium, an indium, a thallium, phosphorus, antimony, a bismuth, sulfur, a selenium, a tellurium, and a polonium.

[0012] The above-mentioned zinc is contained at 7 - 13% of the weight of a rate to tin.

[0013] Moreover, the pewter material of this invention contains tin and the addition component chosen from the group which consists of the zinc, a scandium, an yttrium and a lanthanum, the titanium, the zirconium, the chromium, the iron, the cobalt, the nickel, the copper, the silver, the boron, the aluminum, silicon, and nitrogen of 3 - 21% of the weight of a rate to tin, and this addition component is contained at 0.5 or less % of the weight of a rate to the pewter material whole quantity.

[0014] The above-mentioned zinc is contained at 7 - 13% of the weight of a rate to tin.

[0015] the above-mentioned pewter material -- substantial -- tin-zinc -- duality -- the ratio of eutectic composition -- tin and zinc -- containing -- a content oxygen density -- 1000 ppm It is the following.

[0016] A solder paste is prepared from the above-mentioned pewter material and flux, and flux contains the dissolution or the component which decomposes or returns, and a binder for a metallic oxide.

[0017]

[Embodiments of the Invention] It is obtained when a solder paste mixes the pewter powder which granulated the pewter which carried out heating fusion and prepared two or more sorts of metals, and the flux prepared separately, and junction is formed with the pewter which evaporated or disassembled and flux fused by applying and carrying out a reflow (heating) to the member to solder. the role of flux -- chemical -- a pewter powder front face and the member to solder -- removal, defecation, and the reflow of a surface natural oxidation film -- the member which there is reoxidation prevention in process and is mechanically soldered to the completion of junction -- there is a role which carries out temporary fixation of the comrades Therefore, fundamentally, the dissolution, or the component and binder (binder) component which decomposes or returns

turns into an indispensable component of flux in a metallic oxide.

[0018] Since tin and zinc are the high metals of versatility, although a tin-zinc pewter is an economical very advantageous cementing material, since a problem is in shelf life when it prepares to a solder paste, improvement in the stability of a tin-zinc pewter is required. If the solder paste of a tin-zinc pewter is prepared in detail using the flux used for the conventional tin / lead pewter, compared with the case of tin / lead pewter, the viscosity of a solder paste will rise rapidly, it will harden mostly in about one month after manufacture, and it will become difficult to use it. That is, the shelf life of a solder paste is a low. As this cause, oxidization of the pewter by a small amount of oxygen currently mixed in a reaction and combination with a pewter component and the organic component of flux, a solvent, etc. can be considered. Since the thin film which zinc condensed is formed in a front face in case the fused pewter solidifies a tin-zinc pewter, the reactant high zinc of a pewter particle front face tends to react with flux, and the stability of a solder paste is considered to be a low.

[0019] Moreover, progress of time sees the phenomenon in which the property of a pewter changes, also about the pewter after a reflow. It is thought that this is because an internal state changes with natural aging etc., for example, a fall, an embrittlement, etc. of the elongation of a pewter happen. It is also required to decrease aging of the pewter after such junction.

[0020] In this invention, improvement in the shelf life of the prepared solder paste and suppression of aging of the pewter after junction are aimed at by adding a little addition component to a tin-zinc pewter.

[0021] In order to raise the shelf life of a solder paste, a solid-state component with vapor pressure higher than zinc is used as an addition component (it is also henceforth called the 1st addition component). Specifically, beryllium, magnesium, calcium, strontium, barium, manganese, a gallium, an indium, a thallium, phosphorus, antimony, a bismuth, sulfur, a selenium, a tellurium, a polonium, etc. are mentioned. If these addition components are added to a tin-zinc pewter, it will be thought that the stability of a pewter and the shelf life of an addition component of a solder paste increase when it is easy to exude on the front face of a melting pewter when a pewter is fused, and the outside of the zinc condensed on the front face is covered, or it comes to coexist with zinc and the reaction of reactant high zinc and reactant high flux is delayed. Although the effect which improves the shelf life of the solder paste by addition of the 1st addition component is clear at about 0.1 % of the weight, and an effect will also increase if an addition is increased, if it adds so much, the melting temperature of pewter material becomes low superfluously, and a low melting point phase will be formed. Furthermore, since it separates from the property of a tin-zinc pewter, in order to be the good pewter material which harnessed the advantage of a tin-zinc pewter, it is good to make [of the pewter material whole quantity] the loadings of an addition component into 0.5 or less % of the weight preferably 1 or less % of the weight. Moreover, the fatigue strength in the thermo-cycle examination of pewter material etc. also falls by the superfluous addition component. Since it is an advantage that, as for a tin-zinc pewter, the melting point can set up soldering temperature low in eutectic composition, tin and zinc are blended at a rate near eutectic composition, and a suitable pewter will be obtained if the addition component of the above 1st is added so that it may become 0.5 or less % of the weight of the whole quantity.

[0022] As an addition component (it is also hereafter called the 2nd addition component) which suppresses aging of the tin-zinc pewter after junction, a scandium, an yttrium, a lanthanum, titanium, a zirconium, chromium, iron, cobalt, nickel, copper, silver, boron, aluminum, silicon, and nitrogen are used. These are considered to suppress change of the mechanical characteristic by organization change with time by becoming a nucleus, turning crystal grain minutely and suppressing an internal crystal growth, in case a pewter solidifies by forming tin or zinc, and a compound etc. If the amount of an addition component is little, it will distribute in [whole] a tin-zinc pewter and an addition component will act effective in detailed-izing of an organization--if it exists so much, since the property of a pewter will be mutated by growth of a different-species phase etc., in order that [however,] the loadings of the 2nd addition component may acquire an effect, without spoiling the property of a tin-zinc pewter -- the pewter material whole quantity -- it takes preferably for 0.5 or less % of the weight 1 or less % of the weight

[0023] A property almost of the same grade as tin-zinc eutectic composition (tin : zinc = 91:9 (weight ratio)) is demonstrated, and above-mentioned pewter material can bring soldering temperature or reflow temperature close to eutectic-point temperature, when the rate of the zinc to tin blends so that it may become 7 - 13 % of the weight preferably three to 21% of the weight. The amount of content oxygen of the pewter material from which

manufacture of pewter material, especially melting and a mixed process are acquired since melting temperature will rise rapidly and wettability, intensity, etc. will fall extremely if pewter material oxidizes is 1000 ppm. It is desirable to carry out preventing oxidization using non-oxidizing atmospheres, such as nitrogen, so that it may become the following.

[0024] The prepared pewter material is processed into a line pewter or pewter powder using the usual prescription if needed. Pewter powder serves as a solder paste by mixing with flux. If needed, flux blends various matter and is constituted to make a chemical operation and a mechanical work discover efficiently. Generally, the principal component which constitutes flux is the resin which covers pewter powder and the front face of a member to solder, and has denaturation rosin, a rosin ester, etc. which the rosin system resin (turpentine) which makes an abietic acid etc. a principal component is used, for example, are obtained from a gum rosin, a wood rosin, a tall rosin, and these. A rosin system resin also bears a chemical operation of flux. Thermoplastic synthetic resin, such as polyester resin and acrylic resin, is also used. A solder paste is prepared by selecting suitably the solvent for making such a resinous principle dissolve and mix the CHIKISO agent for holding an auxiliary activator, printing nature as a paste, etc. which assist an operation of the activator for compensating a chemical operation of the pure force of a resin etc. and raising the junction nature of a pewter and an activator, and these etc., and adding. An amine compound etc. is added, in order to add an organic acid, to adjust pH for giving gloss to a pewter, to prevent sagging and to form a pewter ball. As what is generally used well, there are organic acids, such as a halide-acid salt of amine compounds, such as amine compounds, such as a monoethanolamine, a stearyl amine, and a diphenylamine, an ethylamine, propylamine, a diethylamine, and an aniline, a citric acid, a lactic acid, an adipic acid, and stearin acid, etc. In this invention, such a component generally used can be combined suitably if needed, flux can be prepared, it mixes with pewter powder, and a solder paste is obtained. Shelf life of the solder paste by the pewter material which blended the 1st addition component of this invention improves, and offer of the solder paste which can be saved one to three months or more of it is also attained.

[0025] the member which solders the solder paste prepared as mentioned above -- after using and applying technology, such as a screen-stencil method, upwards, make the member to join counter, it is made to contact, and a reflow is performed heating in temperature of about 100-170 degrees C in a reflow process -- above-mentioned flux -- the front face of pewter powder -- being activated -- pewter powder and a member -- a front face contacts Then, pewter powder fuses by heating to the reflow temperature which a pewter fuses. By cooling after this, a metal member is joined with a pewter. If it is desirable above 200 degrees C that it is 10 or less seconds at 30 or less seconds and 240 degrees C as for time to heat to reflow temperature and heating is continued more than required, oxidization of a pewter will tend to advance. Although a reflow can also be carried out in air atmosphere, it is desirable to carry out by the non-oxidizing atmosphere. In a reflow in a non-oxidizing atmosphere, since the piece of the tin-zinc alloy in a melting state or low viscosity is maintained by antioxidizing of pewter powder, it can respond also to formation of precise junction like junction of a high-density-assembly substrate.

[0026] The solder plague of this invention is applicable also about junction of members, such as not only the metal member of single kinds, such as copper, silver, gold, nickel, aluminum, and SUS stainless steel, but an alloy, compound metal material, etc. Moreover, it can respond also to a minute soldered joint enough, and can respond to the soldered joint of the member line breadth and whose line interval are about 0.3mm in the metal member of the shape of a thin line which has a narrow interval. Therefore, it can be used for mounting of a substrate, or the soldered joint for junction of various electric electronic parts. As an example of electric electronic parts, the radiator of the electrical circuit of the current carrying part of the IC package and CPU which are used in a semiconductor field, the hard disk built in a personal computer, and a liquid crystal panel, an IC card, the cable connector used for connection of a personal computer and a printer, the optical connector used for the cable for communication, and an automobile etc. is mentioned. Although the mounting gestalt of a substrate has an one side surface mount, a double-sided surface mount, an element placement with a double-sided surface mount lead, an element placement with an one side surface mount lead, read through mounting, etc., the jointing material of this invention can be used also in any. Moreover, as mounting parts, the ceramic condenser as a passive component, an inductor, a jumper, a transistor, diode, an aluminium electrolytic condenser, tantalum semipermanent resistance, a trimer, a coil, etc. are mentioned, and IC, SI, etc. are the

examples of representation as active parts. As a package configuration, the high-density chip which repeats SOIC, SOP, QIP, QFP, PLCC, LCC, SOJ, MSP and BGA, FC-BGA, CSP, PLC and MCM, OE-MCM, and two or more chips is mentioned.

[0027] According to the quality of the material of the member to join, a precoat may be beforehand given to a member and composition and the precoat method of a precoat can be chosen suitably.

[0028] In a reflow process, if a reducing atmosphere is used, it is still more effective. As a reducing atmosphere, the atmosphere which carried out optimum dose content of the gas-like matter which has reducing is mentioned to inert gas, such as nitrogen, and acid steams, such as alcoholic steams, such as a hydrogen; methanol steam, an ethanol steam, and a propanol steam, formic acid, and an acetic acid, etc. are mentioned to the gas-like matter which has reducing.

[0029] Even if it passes through the tin-zinc pewter using the 2nd addition component from the cooling solidification after a reflow for a long time, it has little systematic change, and the good soldered joint section of elongation is obtained.

[0030] As mentioned above, if the solder paste of this invention is used, the parts by the high tin-zinc system pewter of the versatility which does not contain lead are joinable using the equipment for a solder paste and the facility which are used in the assembly manufacturing process of the present electrical and electric equipment and electronic assembly.

[0031]

[Example] Hereafter, an example explains this invention in detail.

[0032] (Example 1) 100 ppm of oxygen densities In the following nitrogen-gas-atmosphere mind, the tin 91.0 weight section of 99.98% of purity, the zinc 8.5 weight section of 99.99% of purity, and the magnesium 0.5 weight section of 99.97% of purity were supplied to the melting basin, heating fusion was carried out, and it was made uniform. Pewter powder was prepared by making this emit intermittently through a nozzle with a diameter of 50 micrometers, forming a drop, and carrying out cooling solidification in nitrogen-gas-atmosphere mind. This was classified and the pewter powder whose grain size is about 10-50 micrometers was obtained.

[0033] On the other hand, it cooled, after heating mixing the polymerization rosin (turpentine) 46 weight section, the solvent (principal component : terpineol) 44.5 weight section, the hydrogenated-castor-oil (CHIKISO agent) 8 weight section, the activator (principal component : diphenylguanidine hydrobromate) 0.9 weight section, the palmitic-acid 0.3 weight section, and the ethylamine hydrochloride 0.3 weight section, and homogeneous flux was prepared. Stirring mixture of this flux 10 weight section and the above-mentioned pewter powder 90 weight section was carried out in nitrogen-gas-atmosphere mind, and the solder paste was obtained.

[0034] When it took out after saving this solder paste in a refrigerator (5 degrees C) for 60 days, and viscosity was measured, it stopped at 5% of increase from early viscosity, and was in the state usable enough.

[0035] Furthermore, when IC parts on a 5mmx0.5mm copper pad were soldered on the following reflow conditions using this solder paste, the pewter fused at the reflow temperature of 200-205 degrees C. When the following thermo-cycle examinations were carried out about the soldering part immediately after cooling, the problem did not have after 1000 cycle progress in any way.

[0036] [Reflow conditions]

Reflow time: 6 minutes, preheating temperature: 150 degree C, maximum-heating-temperature: 228 degree C, furnace atmosphere: nitrogen supply, 500 ppm [a thermo-cycle examination] of oxygen densities

temperature requirement: -- number of -50 degrees C - +150 degree-C cycles: -- 1000 cycle [0037] (Example 2)

After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used calcium of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0038] (Example 3) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used barium of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0039] (Example 4) After having replaced with magnesium, having repeated the same operation as an example

1, preparing the solder paste except having used manganese of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0040] (Example 5) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used the indium of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0041] (Example 6) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used the phosphorus of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0042] (Example 7) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used sulfur of 99.99% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0043] (Example 8) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used the bismuth of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0044] (Example 1 of comparison) 100 ppm of oxygen densities In the following nitrogen-gas-atmosphere mind, the tin 91.0 weight section of 99.98% of purity and the zinc 9.0 weight section of 99.99% of purity are supplied to a melting basin, and heating fusion is carried out. This part is supplied to a mold, and it cools, and is JIS. When two pieces of 140mmx18mmx3mm pieces of a pewter according to 13B test piece of Z2201 were created and the elongation of the piece of a pewter immediately after creation and of ten days after was measured, they were 52.2% and 46.2%.

[0045] Using the remainder of a melt, the solder paste was prepared like the example 1, the copper pad was joined by solder like the example 1 using this part, and other portions were similarly saved in the refrigerator on the 45th.

[0046] When joining by solder, and the pewter fused in the stage where reflow temperature is 199 degrees C and the thermo-cycle examination of a soldering part was carried out on condition that the example 1 after cooling, it was satisfactory in any way.

[0047] Moreover, when the solder paste after saving in a refrigerator was taken out, it had hardened and was not able to print by predetermined thickness from a metal mask.

[0048] (Example 2 of comparison) After having repeated the same operation as an example 1, preparing the solder paste except having changed the amount of the 90.5 weight sections and magnesium into the 1.0 weight section for the amount of the used tin and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the usable state.

[0049] furthermore, this solder paste -- using -- copper -- when junction by soldering of a member was tried, the pewter fused in the stage where reflow temperature is 200-208 degrees C When the thermo-cycle examination of a soldering part was carried out on condition that the example 1 immediately after cooling, the defect was found at 3% of a rate after the 1000 cycle end.

[0050] (Example 9) 100 ppm of oxygen densities In the following nitrogen-gas-atmosphere mind, the tin 91.0 weight section of 99.98% of purity, the zinc 8.5 weight section of 99.99% of purity, and the aluminum 0.5 weight section of 99.97% of purity were supplied to the melting basin, heating fusion was carried out, and it was made uniform. A part of this melt is supplied to a mold, and it cools, and is JIS. When two pieces of 140mmx18mmx3mm pieces of a pewter according to 13B test piece of Z2201 were created and the elongation of the piece of a pewter immediately after creation and of ten days after was measured, it was immediately after creation and was 53.5% after 53.5% and ten days.

[0051] When the solder paste was prepared like the example 1 using the remainder of a melt, the copper pad was joined and the thermo-cycle examination was carried out on the same conditions as an example 1, it was satisfactory in any way.

[0052] (Example 10) Except having replaced with aluminum and having used titanium of 99.97% of purity, when the piece of a pewter was created by the same operation as an example 9 and the elongation immediately after creation and of ten days after was measured respectively, it was immediately after creation and was 53.8% after 53.8% and ten days.

[0053] (Example 11) Except having replaced with aluminum and having used silicon of 99.97% of purity, when the piece of a pewter was created by the same operation as an example 9 and the elongation immediately after creation and of ten days after was measured respectively, it was immediately after creation and was 54.5% after 54.5% and ten days.

[0054] (Example 12) Except having replaced with aluminum and having used the yttrium of 99.97% of purity, when the same operation as an example 9 was repeated, the piece of a pewter was created and the elongation immediately after creation and of ten days after was measured respectively, it was immediately after creation and was 54.0% after 54.0% and ten days.

[0055]

[Effect of the Invention] According to this invention, the shelf life of a solder paste which the tin-zinc pewter using the little addition component added flux, and was prepared is improved. Moreover, aging, such as the mechanical characteristic of the soldered joint after junction, can be suppressed. Therefore, the problem of lead effective [very] and contained in waste for utilization of the tin-zinc pewter which does not contain lead, is solvable. Therefore, this invention is very useful on industry and an environmental cure.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the pewter material which does not contain the lead for joining the electrical and electric equipment, an electron, or a machine part. In detail, it is related with the pewter material containing the joinable tin and joinable zinc of a high metallic material of the versatility of the electrical and electric equipment or electronic parts, such as the circuit board, stainless steel, etc.

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PRIOR ART

[Description of the Prior Art] Soldering is the technology in which the melting point joins bodies using the comparatively low matter, it is used for many years and it is said that the origin can go back to the old Mesopotamia civilization. In present-day industry, soldering is broadly used for junction of electronic equipment, and assembly. For example, it is used for the junction for mounting electronic parts, such as a semiconductor, a microprocessor, memory, and resistance, in a substrate etc. in the mounting substrate. The advantage of soldering is that electrical installation is formed of the conductivity of the metal contained in a pewter, and it not only fixes parts to a substrate, but differs from the adhesives of an organic system in this point.

[0003] Since the pewter generally used is lower than the temperature to which it is a eutectic pewter by tin and lead, the theoretical eutectic point is 183 degrees C, and much thermosetting resin begins gasification, tin / lead eutectic pewter is used for junction of a substrate etc., and it has the feature that it is not necessary to damage a printed circuit board etc. with heat. Moreover, a tin component forms a characteristic metallic-compounds layer by the interface of a copper plate, and, as for this eutectic pewter, strengthening adhesive strength of a pewter and copper more is also known.

[0004] The eutectic pewter by tin and lead equipped with such a feature is important in junction of the parts in manufacture of electronic equipment, and assembly. thick-film formation and a conductor -- in detailed soldering processing like circuit formation and semiconductor mounting, the screen-stencil method using the solder paste of the shape of a paste which mixed pewter powder and flux etc. is used, and the need of the pewter in the mounting technology of electronic parts is growing increasingly as the rapid spread of the personal devices represented by a personal computer, a cellular phone, the pager, etc. progresses

[0005] The spread of electronic equipment lives a life of people rich. On the other hand, it is also a fact that the electronic equipment which it stopped using is discarded so much, and it is doubtful of the environmental problem by waste arising. For this reason, the manufacture method of not using recycling use or the detrimental matter of waste is advocated. From a viewpoint of preventing environmental pollution, especially exclusion of a toxic substance is desirable and it is thought also in the junction technology by the pewter that it needs development.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the shelf life of a solder paste which the tin-zinc pewter using the little addition component added flux, and was prepared is improved. Moreover, aging, such as the mechanical characteristic of the soldered joint after junction, can be suppressed. Therefore, the problem of lead effective [very] and contained in waste for utilization of the tin-zinc pewter which does not contain lead, is solvable. Therefore, this invention is very useful on industry and an environmental cure.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although tin / lead eutectic pewter has the special feature that the wettability to a base material is superior to other metal mixture, when the lead contained in this pewter reclaimed land from and disposes of the discarded electronic equipment, we are anxious about lead ion being eluted into soil by being exposed to acid rain etc. over many years. Since it corresponds to this, although the technology which fixes lead is proposed, sufficient data over a long period of time are not obtained about diffusion into soil. Furthermore, according to the densification of the latest memory device, a close-up of the influence on the electronic equipment by lead is taken, and reexamination is [as opposed to / leaden use / from the field of the correspondence to the high density assembly in a semiconductor device] needed.

[0007] From such a situation, the junction technology using the pewter which does not contain lead is needed. However, since neither the pewter which replaced lead with other metals, nor the pewter by the combination of another metal becomes so sufficient that it is used so much as a general-purpose product thing about the property needed for pewters, such as wettability, soldering temperature, material strength, and economical efficiency, it is a grade it is expected that the use which did not yet result in spread but was limited to the specific use is.

[0008] Since equipment and the facility of a screen-stencil method using a solder paste have permeated the manufacture site in junction and assembly of the electrical and electric equipment and electronic parts in the present condition, utilization of the solder paste of the pewter which does not contain lead is called for. However, now, most unleaded solder pastes are not put [that utilization of the solder paste in the pewter of complicated 3 yuan or more systems, such as tin / silver / bismuth pewter, is only tried slightly, and] in practical use. It is mentioned that the solder paste which has the shelf life of this reason satisfied with one is not obtained. Furthermore, there are also problems, such as aging of the pewter after junction, i.e., change of a mechanical characteristic etc.

[0009]

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MEANS

[Means for Solving the Problem] Then, in order that this invention persons may solve the environmental problem by the lead in waste As a result of repeating research wholeheartedly about soldering using the pewter by the high metal of the versatility which does not contain lead, by carrying out minute amount addition of the specific third component It finds out that improvement in the stability of the tin-zinc pewter at the time of preparing to a solder paste and aging of the tin-zinc pewter after junction can be suppressed, and came to complete the pewter material of this invention.

[0010] The pewter material of this invention is [in / the zinc and the ordinary temperature ordinary pressure of 3 - 21% of the weight of a rate / to tin and tin] a solid-state, an addition component with vapor pressure higher than zinc is contained, and this addition component is contained at 0.5 or less % of the weight of a rate to the pewter material whole quantity.

[0011] The above-mentioned addition component is chosen from the group which consists of beryllium, magnesium, calcium, strontium, barium, manganese, a gallium, an indium, a thallium, phosphorus, antimony, a bismuth, sulfur, a selenium, a tellurium, and a polonium.

[0012] The above-mentioned zinc is contained at 7 - 13% of the weight of a rate to tin.

[0013] Moreover, the pewter material of this invention contains tin and the addition component chosen from the group which consists of the zinc, a scandium, an yttrium and a lanthanum, the titanium, the zirconium, the chromium, the iron, the cobalt, the nickel, the copper, the silver, the boron, the aluminum, silicon, and nitrogen of 3 - 21% of the weight of a rate to tin, and this addition component is contained at 0.5 or less % of the weight of a rate to the pewter material whole quantity.

[0014] The above-mentioned zinc is contained at 7 - 13% of the weight of a rate to tin.

[0015] the above-mentioned pewter material -- substantial -- tin-zinc -- duality -- the ratio of eutectic composition -- tin and zinc -- containing -- a content oxygen density -- 1000 ppm It is the following.

[0016] A solder paste is prepared from the above-mentioned pewter material and flux, and flux contains the dissolution or the component which decomposes or returns, and a binder for a metallic oxide.

[0017]

[Embodiments of the Invention] It is obtained when a solder paste mixes the pewter powder which granulated the pewter which carried out heating fusion and prepared two or more sorts of metals, and the flux prepared separately, and junction is formed with the pewter which evaporated or disassembled and flux fused by applying and carrying out a reflow (heating) to the member to solder. the role of flux -- chemical -- a pewter powder front face and the member to solder -- removal, defecation, and the reflow of a surface natural oxidation film -- the member which there is reoxidation prevention in process and is mechanically soldered to the completion of junction -- there is a role which carries out temporary fixation of the comrades Therefore, fundamentally, the dissolution, or the component and binder (binder) component which decomposes or returns turns into an indispensable component of flux in a metallic oxide.

[0018] Since tin and zinc are the high metals of versatility, although a tin-zinc pewter is an economical very advantageous cementing material, since a problem is in shelf life when it prepares to a solder paste, improvement in the stability of a tin-zinc pewter is required. If the solder paste of a tin-zinc pewter is prepared in detail using the flux used for the conventional tin / lead pewter, compared with the case of tin / lead pewter, the viscosity of a solder paste will rise rapidly, it will harden mostly in about one month after manufacture, and it will become difficult to use it. That is, the shelf life of a solder paste is low. As this cause, oxidization of the

pewter by a small amount of oxygen currently mixed in a reaction and combination with a pewter component and the organic component of flux, a solvent, etc. can be considered. Since the thin film which zinc condensed is formed in a front face in case the fused pewter solidifies, the reactant high zinc of a pewter particle front face tends to react with flux, and a tin-zinc pewter is considered that the stability of a solder paste is low.

[0019] Moreover, progress of time sees the phenomenon in which the property of a pewter changes, also about the pewter after a reflow. It is thought that this is because an internal state changes with natural aging etc., for example, a fall, an embrittlement, etc. of the elongation of a pewter happen. It is also required to decrease aging of the pewter after such junction.

[0020] In this invention, improvement in the shelf life of the prepared solder paste and suppression of aging of the pewter after junction are aimed at by adding a little addition component to a tin-zinc pewter.

[0021] In order to raise the shelf life of a solder paste, a solid-state component with vapor pressure higher than zinc is used as an addition component (it is also henceforth called the 1st addition component). Specifically, beryllium, magnesium, calcium, strontium, barium, manganese, a gallium, an indium, a thallium, phosphorus, antimony, a bismuth, sulfur, a selenium, a tellurium, a polonium, etc. are mentioned. If these addition components are added to a tin-zinc pewter, it will be thought that the stability of a pewter and the shelf life of an addition component of a solder paste increase when it is easy to exude on the front face of a melting pewter when a pewter is fused, and the outside of the zinc condensed on the front face is covered, or it comes to coexist with zinc and the reaction of reactant high zinc and reactant high flux is delayed. Although the effect which improves the shelf life of the solder paste by addition of the 1st addition component is clear at about 0.1 % of the weight, and an effect will also increase if an addition is increased, if it adds so much, the melting temperature of pewter material becomes low superfluously, and a low melting point phase will be formed. Furthermore, since it separates from the property of a tin-zinc pewter, in order to be the good pewter material which harnessed the advantage of a tin-zinc pewter, it is good to make [of the pewter material whole quantity] the loadings of an addition component into 0.5 or less % of the weight preferably 1 or less % of the weight. Moreover, the fatigue strength in the thermo-cycle examination of pewter material etc. also falls by the superfluous addition component. Since it is an advantage that, as for a tin-zinc pewter, the melting point can set up soldering temperature low in eutectic composition, tin and zinc are blended at a rate near eutectic composition, and a suitable pewter will be obtained if the addition component of the above 1st is added so that it may become 0.5 or less % of the weight of the whole quantity.

[0022] As an addition component (it is also hereafter called the 2nd addition component) which suppresses aging of the tin-zinc pewter after junction, a scandium, an yttrium, a lanthanum, titanium, a zirconium, chromium, iron, cobalt, nickel, copper, silver, boron, aluminum, silicon, and nitrogen are used. These are considered to suppress change of the mechanical characteristic by organization change with time by becoming a nucleus, turning crystal grain minutely and suppressing an internal crystal growth, in case a pewter solidifies by forming tin or zinc, and a compound etc. If the amount of an addition component is little, it will distribute in [whole] a tin-zinc pewter and an addition component will act effective in detailed-izing of an organization. if it exists so much, since the property of a pewter will be mutated by growth of a different-species phase etc., in order that [however,] the loadings of the 2nd addition component may acquire an effect, without spoiling the property of a tin-zinc pewter -- the pewter material whole quantity -- it takes preferably for 0.5 or less % of the weight 1 or less % of the weight

[0023] A property almost of the same grade as tin-zinc eutectic composition (tin : zinc = 91:9 (weight ratio)) is demonstrated, and above-mentioned pewter material can bring soldering temperature or reflow temperature close to eutectic-point temperature; when the rate of the zinc to tin blends so that it may become 7 - 13 % of the weight preferably three to 21% of the weight. The amount of content oxygen of the pewter material from which manufacture of pewter material, especially melting and a mixed process are acquired since melting temperature will rise rapidly and wettability, intensity, etc. will fall extremely if pewter material oxidizes is 1000 ppm. It is desirable to carry out preventing oxidization using non-oxidizing atmospheres, such as nitrogen, so that it may become the following.

[0024] The prepared pewter material is processed into a line pewter or pewter powder using the usual prescription if needed. Pewter powder serves as a solder paste by mixing with flux. If needed, flux blends various matter and is constituted to make a chemical operation and a mechanical work discover efficiently.

Generally, the principal component which constitutes flux is the resin which covers pewter powder and the front face of a member to solder, and has denaturation rosin, a rosin ester, etc. which the rosin system resin (turpentine) which makes an abietic acid etc. a principal component is used, for example, are obtained from a gum rosin, a wood rosin, a tall rosin, and these. A rosin system resin also bears a chemical operation of flux. Thermoplastic synthetic resin, such as polyester resin and acrylic resin, is also used. A solder paste is prepared by selecting suitably the solvent for making such a resinous principle dissolve and mix the CHIKISO agent for holding an auxiliary activator, printing nature as a paste, etc. which assist an operation of the activator for compensating a chemical operation of the pure force of a resin etc. and raising the junction nature of a pewter and an activator, and these etc., and adding. An amine compound etc. is added, in order to add an organic acid, to adjust pH for giving gloss to a pewter, to prevent sagging and to form a pewter ball. As what is generally used well, there are organic acids, such as a halide-acid salt of amine compounds, such as amine compounds, such as a monoethanolamine, a stearyl amine, and a diphenylamine, an ethylamine, propylamine, a diethylamine, and an aniline, a citric acid, a lactic acid, an adipic acid, and stearin acid, etc. In this invention, such a component generally used can be combined suitably if needed, flux can be prepared, it mixes with pewter powder, and a solder paste is obtained. Shelf life of the solder paste by the pewter material which blended the 1st addition component of this invention improves, and offer of the solder paste which can be saved one to three months or more of it is also attained.

[0025] the member which solders the solder paste prepared as mentioned above -- after using and applying technology, such as a screen-stencil method, upwards, make the member to join counter, it is made to contact, and a reflow is performed heating in temperature of about 100-170 degrees C in a reflow process -- above-mentioned flux -- the front face of pewter powder -- being activated -- pewter powder and a member -- a front face contacts Then, pewter powder fuses by heating to the reflow temperature which a pewter fuses. By cooling after this, a metal member is joined with a pewter. If it is desirable above 200 degrees C that it is 10 or less seconds at 30 or less seconds and 240 degrees C as for time to heat to reflow temperature and heating is continued more than required, oxidization of a pewter will tend to advance. Although a reflow can also be carried out in air atmosphere, it is desirable to carry out by the non-oxidizing atmosphere. In a reflow in a non-oxidizing atmosphere, since the piece of the tin-zinc alloy in a melting state or low viscosity is maintained by antioxidizing of pewter powder, it can respond also to formation of precise junction like junction of a high-density-assembly substrate.

[0026] The solder plague of this invention is applicable also about junction of members, such as not only the metal member of single kinds, such as copper, silver, gold, nickel, aluminum, and SUS stainless steel, but an alloy, compound metal material, etc. Moreover, it can respond also to a minute soldered joint enough, and can respond to the soldered joint of the member line breadth and whose line interval are about 0.3mm in the metal member of the shape of a thin line which has a narrow interval. Therefore, it can be used for mounting of a substrate, or the soldered joint for junction of various electric electronic parts. As an example of electric electronic parts, the radiator of the electrical circuit of the current carrying part of the IC package and CPU which are used in a semiconductor field, the hard disk built in a personal computer, and a liquid crystal panel, an IC card, the cable connector used for connection of a personal computer and a printer, the optical connector used for the cable for communication, and an automobile etc. is mentioned. Although the mounting gestalt of a substrate has an one side surface mount, a double-sided surface mount, an element placement with a double-sided surface mount lead, an element placement with an one side surface mount lead, read through mounting, etc., the jointing material of this invention can be used also in any. Moreover, as mounting parts, the ceramic condenser as a passive component, an inductor, a jumper, a transistor, diode, an aluminium electrolytic condenser, tantalum semipermanent resistance, a trimer, a coil, etc. are mentioned, and IC, SI, etc. are the examples of representation as active parts. As a package configuration, the high-density chip which repeats SOIC, SOP, QIP, QFP, PLCC, LCC, SOJ, MSP and BGA, FC-BGA, CSP, PLC and MCM, OE-MCM, and two or more chips is mentioned.

[0027] According to the quality of the material of the member to join, a precoat may be beforehand given to a member and composition and the precoat method of a precoat can be chosen suitably.

[0028] In a reflow process, if a reducing atmosphere is used, it is still more effective. As a reducing atmosphere, the atmosphere which carried out proper quantity content of the gas-like matter which has reducing is

mentioned to inert gas, such as nitrogen, and acid steams, such as alcoholic steams, such as a hydrogen; methanol steam, an ethanol steam, and a propanol steam, formic acid, and an acetic acid, etc. are mentioned to the gas-like matter which has reducing.

[0029] Even if it passes through the tin-zinc pewter using the 2nd addition component from the cooling solidification after a reflow for a long time, it has little systematic change, and the good soldered joint section of elongation is obtained.

[0030] As mentioned above, if the solder paste of this invention is used, the parts by the high tin-zinc system pewter of the versatility which does not contain lead are joinable using the equipment for a solder paste and the facility which are used in the assembly manufacturing process of the present electrical and electric equipment and electronic assembly.

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EXAMPLE

[Example] Hereafter, an example explains this invention in detail.

[0032] (Example 1) 100 ppm of oxygen densities In the following nitrogen-gas-atmosphere mind, the tin 91.0 weight section of 99.98% of purity, the zinc 8.5 weight section of 99.99% of purity, and the magnesium 0.5 weight section of 99.97% of purity were supplied to the melting basin, heating fusion was carried out, and it was made uniform. Pewter powder was prepared by making this emit intermittently through a nozzle with a diameter of 50 micrometers, forming a drop, and carrying out cooling solidification in nitrogen-gas-atmosphere mind. This was classified and the pewter powder whose grain size is about 10-50 micrometers was obtained.

[0033] On the other hand, it cooled, after heating mixing the polymerization rosin (turpentine) 46 weight section, the solvent (principal component : terpineol) 44.5 weight section, the hydrogenated-castor-oil (CHIKISO agent) 8 weight section, the activator (principal component : diphenylguanidine hydrobromate) 0.9 weight section, the palmitic-acid 0.3 weight section, and the ethylamine hydrochloride 0.3 weight section, and homogeneous flux was prepared. Stirring mixture of this flux 10 weight section and the above-mentioned pewter powder 90 weight section was carried out in nitrogen-gas-atmosphere mind, and the solder paste was obtained.

[0034] When it took out after saving this solder paste in a refrigerator (5 degrees C) for 60 days, and viscosity was measured, it stopped at 5% of increase from early viscosity, and was in the state usable enough.

[0035] Furthermore, when IC parts on a 5mmx0.5mm copper pad were soldered on the following reflow conditions using this solder paste, the pewter fused at the reflow temperature of 200-205 degrees C. When the following thermo-cycle examinations were carried out about the soldering part immediately after cooling, the problem did not have after 1000 cycle progress in any way.

[0036] [Reflow conditions]

Reflow time: 6 minutes, preheating temperature: 150 degree C, maximum-heating-temperature: 228 degree C, furnace atmosphere: nitrogen supply, 500 ppm [a thermo-cycle examination] of oxygen densities

temperature requirement: -- number of -50 degrees C - +150 degree-C cycles: -- 1000 cycle [0037] (Example 2)

After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used calcium of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state..

[0038] (Example 3) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used barium of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0039] (Example 4) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used manganese of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0040] (Example 5) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used the indium of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0041] (Example 6) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used the phosphorus of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0042] (Example 7) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used sulfur of 99.99% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0043] (Example 8) After having replaced with magnesium, having repeated the same operation as an example 1, preparing the solder paste except having used the bismuth of 99.97% of purity and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the sufficiently usable state.

[0044] (Example 1 of comparison) 100 ppm of oxygen densities In the following nitrogen-gas-atmosphere mind, the tin 91.0 weight section of 99.98% of purity and the zinc 9.0 weight section of 99.99% of purity are supplied to a melting basin, and heating fusion is carried out. This part is supplied to a mold, and it cools, and is JIS. When two pieces of 140mmx18mmx3mm pieces of a pewter according to 13B test piece of Z2201 were created and the elongation of the piece of a pewter immediately after creation and of ten days after was measured, they were 52.2% and 46.2%.

[0045] Using the remainder of a melt, the solder paste was prepared like the example 1, the copper pad was joined by solder like the example 1 using this part, and other portions were similarly saved in the refrigerator on the 45th.

[0046] When joining by solder, and the pewter fused in the stage where reflow temperature is 199 degrees C and the thermo-cycle examination of a soldering part was carried out on condition that the example 1 after cooling, it was satisfactory in any way.

[0047] Moreover, when the solder paste after saving in a refrigerator was taken out, it had hardened and was not able to print by predetermined thickness from a metal mask.

[0048] (Example 2 of comparison) After having repeated the same operation as an example 1, preparing the solder paste except having changed the amount of the 90.5 weight sections and magnesium into the 1.0 weight section for the amount of the used tin and saving in a refrigerator similarly for 60 days, when it took out, viscosity stopped at 5% of increase from early viscosity, and was in the usable state.

[0049] furthermore, this solder paste -- using -- copper -- when junction by soldering of a member was tried, the pewter fused in the stage where reflow temperature is 200-208 degrees C When the thermo-cycle examination of a soldering part was carried out on condition that the example 1 immediately after cooling, the defect was found at 3% of a rate after the 1000 cycle end.

[0050] (Example 9) 100 ppm of oxygen densities In the following nitrogen-gas-atmosphere mind, the tin 91.0 weight section of 99.98% of purity, the zinc 8.5 weight section of 99.99% of purity, and the aluminum 0.5 weight section of 99.97% of purity were supplied to the melting basin, heating fusion was carried out, and it was made uniform. A part of this melt is supplied to a mold, and it cools, and is JIS. When two pieces of 140mmx18mmx3mm pieces of a pewter according to 13B test piece of Z2201 were created and the elongation of the piece of a pewter immediately after creation and of ten days after was measured, it was immediately after creation and was 53.5% after 53.5% and ten days.

[0051] When the solder paste was prepared like the example 1 using the remainder of a melt, the copper pad was joined and the thermo-cycle examination was carried out on the same conditions as an example 1, it was satisfactory in any way.

[0052] (Example 10) Except having replaced with aluminum and having used titanium of 99.97% of purity, when the piece of a pewter was created by the same operation as an example 9 and the elongation immediately after creation and of ten days after was measured respectively, it was immediately after creation and was 53.8% after 53.8% and ten days.

[0053] (Example 11) Except having replaced with aluminum and having used silicon of 99.97% of purity, when the piece of a pewter was created by the same operation as an example 9 and the elongation immediately after creation and of ten days after was measured respectively, it was immediately after creation and was 54.5% after

54.5% and ten days.

[0054] (Example 12) Except having replaced with aluminum and having used the yttrium of 99.97% of purity, when the same operation as an example 9 was repeated, the piece of a pewter was created and the elongation immediately after creation and of ten days after was measured respectively, it was immediately after creation and was 54.0% after 54.0% and ten days.

[Translation done.]